Photodissociation in Quantum Chaotic Systems: Random Matrix Theory of Cross-Section Fluctuations

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Using the random matrix description of open quantum chaotic systems we calculate in closed form the universal autocorrelation function and the probability distribution of the total photodissociation cross section in the regime of quantum chaos.

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Recent advances in laser techniques allow precision measurements of the photodissociation of polyatomic molecules [1]. Realistic quantum calculations of the photodissociation spectra for small polyatomic molecules, such as the radicals HO_2 and NO_2 [1] or the H_3^+ molecular ion [2] are also becoming available. The photodissociation describes the breakup of a bound molecule by the absorption of photons, and usually proceeds through excited intermediate resonance states. These resonance states are directly coupled to the continuum states that describe possible breakup channels of the molecule into fragments, and their properties are expected to play a major role in the dissociation process. Resonances are characteristic of all kinds of open systems, i.e. systems in which motion along some directions is unbound.

One of the important observables is the total photodissociation cross-section. Often it exhibits irregular fluctuations consisting of partly overlapping peaks (e.g. see [1] for the molecule HO_2) . Similar fluctuation patterns were first observed in resonance neutron scattering [3] and are typical for many other systems such as heavy ions [4] and atoms [5]. The statistics of the neutron resonance data was explained by random matrix theory (RMT) [3], where the Hamiltonian is assumed to satisfy the underlying fundamental symmetries of the system but is otherwise random. Originally justified by the complexity of the nuclear system, RMT was later understood to be applicable in systems whose underlying classical dynamics is chaotic [6]. Such chaotic systems are expected to exhibit fluctuations whose statistical properties are universal, i.e. common to systems of different physical nature and depending only on the symmetry class. RMT was successfully applied in the description of both bound and open quantum chaotic systems [7]. Several universal features of chaotic scattering were recently calculated in closed form; see Ref. [8] for details. We therefore expect that the photodissociation cross-section of chaotic systems will also display universal features. Here we derive closed expressions for the the autocorrelation function and distribution of the total photodissociation cross-section in open chaotic systems.

Following the absorption of a photon, the excited molecule can dissociate into several channels. A channel describes a fragmentation of the system into several (possibly excited) fragments whose relative motion is described by a superposition of incoming and outgoing spherical waves. We assume that at given energy E there are M different possible open channels. A dissociation solution $\Phi_c(E)$ to the Schrödinger equation is defined as a solution that satisfies the following boundary conditions: an outgoing wave in exactly one open channel c, and incoming waves in all channels. At the given energy E there are exactly M independent dissociation solutions Φ_c $(c = 1, 2, \ldots, M)$. The total cross section $\sigma(E)$ for the molecule in its ground state $|g\rangle$ (or more generally any bound state) to absorb a photon of energy $E - E_g$ and to dissociate into any of its M open channels is given, in the dipole approximation, by

$$\sigma(E) = \sigma_0 \sum_c |\langle \Phi_c(E)|\mu|g\rangle|^2 \ , \tag{1}$$

Here $\hat{\mu} = \boldsymbol{\mu} \cdot \hat{\mathbf{e}}$ is the component of dipole moment $\boldsymbol{\mu}$ of the system along the polarization $\hat{\mathbf{e}}$ of the absorbed light, and $\sigma_0 = (2\hbar^2\epsilon_0 c)^{-1}(E - E_g)$.

To incorporate RMT description into scattering theory [7,8] it is convenient to divide the Hilbert space of the dissociating system into two parts [9]: the internal "interaction" region, and the external "channel" region where the fragments are far enough from each other that their interaction can be neglected. Any solution $\Phi(E)$ at energy E can then be represented in terms of its components $\mathbf{u}$ and ψ, inside the interaction region and channel region, respectively. Using standard methods of scattering theory (see e.g. [8,10]) one can relate the M outgoing amplitudes of ψ (denoted by the M-component vector $\mathbf{B}$) to the inside components $\mathbf{u}$ by a linear relation $\mathbf{u} = \hat{\mathbf{C}}\mathbf{B}$, where

$$\hat{\mathbf{C}} = \left(E - H_{in} - i\pi WW^\dagger\right)^{-1} W \ . \tag{2}$$

Here H_{in} is the Hamiltonian describing the *closed* interaction region when it is decoupled from the channel region (e.g. by imposing appropriate boundary conditions), and the operator W describes the coupling between the two parts of the Hilbert space.

Assuming that the classical dynamics of the closed interaction region is fully chaotic, we can replace the actual Hamiltonian H_{in} by a random $N \times N$ matrix taken from the Gaussian orthogonal ensemble (GOE) for systems with preserved time-reversal invariance and from the Gaussian unitary ensemble (GUE) for systems with broken time-reversal symmetry. The coupling W is represented by an $N \times M$ matrix which we consider to be fixed. Because of the invariance of the random matrix Hamiltonian H_{in} under orthogonal (unitary) transformations, the coupling to the channels is essentially characterized by only M invariants, the eigenvalues of $W^\dagger W$. These eigenvalues can be expressed in term of the transmission coefficients T_c ($0 < T_c < 1$), defined through the averaged S-matrix by $T_c = 1 - |\langle S_{cc} \rangle|^2$. The limit $T_c \ll 1$ corresponds to an almost closed channel c, whereas $T_c = 1$ corresponds to the limit of perfect coupling between the interaction region and the channel c.

A central assumption in our model is that direct transitions from the ground state to the channels induced by the transition operator $\hat{\mu}$ are negligible, and thus the decay is possible only via the excited resonance levels. Using this fact and Eq. (2), the total photodissociation cross-section (1) can be rewritten in the following optical theorem form:

$$\sigma(E) \propto \left\langle g \left| \hat{\mu} \hat{\mathbf{C}} \hat{\mathbf{C}}^\dagger \hat{\mu} \right| g \right\rangle \propto \mathrm{Im} \left\langle g \left| \hat{\mu} \frac{1}{E - \mathcal{H}_{eff}} \hat{\mu} \right| g \right\rangle , \quad (3)$$

where $\mathcal{H}_{eff} = H_{in} - i\pi W W^\dagger$ is the effective non-Hermitean Hamiltonian known to describe open chaotic systems. For closed system ($W = 0$), Eq. (3) reduces to the strength function of $\hat{\mu}$, whose statistical properties were studied in Refs. [11,12]. The particular resolvent form (3) has the advantage of being suitable for application of Efetov's supermatrix formalism [13,7]. The detailed presentation of such a calculation can be found in [8], and here we only present the final result for the autocorrelation function of the photodissociation cross-section defined by

$$S\left(\omega = \pi\Omega/\Delta\right) = \frac{\langle \sigma(E - \Omega/2)\sigma(E + \Omega/2) \rangle}{\langle \sigma(E) \rangle^2} - 1 , \quad (4)$$

with Δ being the mean level spacing for the Hamiltonian H_{in}. $S(\omega)$ is found to be a sum of two terms $S(\omega) = S_1(\omega) + S_2(\omega)$, which for the GOE case are given by

$$S_{1,2}(\omega) = \int_{-1}^{1} d\lambda \int_{1}^{\infty} d\lambda_1 \int_{1}^{\infty} d\lambda_2 \frac{\cos\left[\omega(\lambda_1 \lambda_2 - \lambda)\right](1 - \lambda^2)}{[\lambda_1^2 + \lambda_2^2 + \lambda^2 - 2\lambda_1\lambda_2\lambda - 1]^2}$$
$$\times f_{1,2}(\lambda, \lambda_1, \lambda_2) \prod_{c=1}^{M} \frac{(g_c + \lambda)}{[(g_c + \lambda_1\lambda_2)^2 - (\lambda_1^2 - 1)(\lambda_2^2 - 1)]^{1/2}} , \quad (5)$$

where

$$f_1(\lambda, \lambda_1, \lambda_2) = 2\lambda_1^2\lambda_2^2 - \lambda_1^2 - \lambda_2^2 - \lambda^2 + 1;$$

$$f_2(\lambda, \lambda_1, \lambda_2) = (\lambda_1\lambda_2 - \lambda)^2 .$$

The parameters g_c are related to the transmission coefficients by $g_c = 2/T_c - 1$. We note that each of the contributions $S_{1,2}(\omega)$ represents an interesting object by itself; $S_2(\omega)$ coincides with the autocorrelation function of the Wigner time delays (studied in [8,14–16]), whereas $S_1(\omega)$ is related to the Fourier transform of the "norm leakage" out of the interaction region. The latter quantity was introduced recently by Savin and Sokolov as a characteristic of the process of quantum relaxation in chaotic systems [17].

For the GUE case one finds $S(\omega)$ to be

$$S(\omega) = \int_{-1}^{1} d\lambda \int_{1}^{\infty} d\lambda_1 \frac{\lambda_1}{\lambda_1 - \lambda} \prod_{c} \left(\frac{g_c + \lambda}{g_c + \lambda_1} \right) \cos\left[\omega(\lambda_1 - \lambda)\right] . \quad (6)$$

In the limit of a closed system ($T_c = 0$ for all c), the expressions (5) and (6) reduce to the strength function correlators calculated earlier using RMT [11] and the supersymmetry method [12]. This limit corresponds physically to energies E below the threshold for photodissociation (bound-to-bound transitions). Simpler analytic forms can be obtained in various limits, such as the limit of almost closed systems (i.e. all $T_c \ll 1$), and we defer the analysis to a future publication. Here we discuss in detail only the limit of a large number of equivalent dissociation channels ($M \gg 1$, $T_c = T$) and large density of resonances $\rho = 1/\Delta$, where all resonances are found to have the same width Γ [8]. Such an open system is characterized by a single parameter $MT = 2\pi\rho\Gamma \equiv \kappa$, measuring the degree of resonance overlap [14,8,17]. In this limit of homogeneously broadened resonances one finds (cf. [14]):

$$S_1(\omega) = \frac{2}{\beta} \frac{\kappa/2}{\omega^2 + \kappa^2/4} \quad (7)$$
$$S_2(\omega) = \frac{\kappa/2}{\omega^2 + \kappa^2/4} - \int_{-\infty}^{\infty} d\tilde{\omega} Y_{2,\beta}(\tilde{\omega}) \frac{\kappa/(2\pi)}{(\omega - \tilde{\omega})^2 + \kappa^2/4} , \quad (8)$$

where $Y_{2,\beta}(\omega)$ is Dyson's two-level correlation function and $\beta = 1, 2$ for the GOE and GUE cases, respectively. For strongly overlapping resonances, i.e. $\kappa \gg 1$, the function $S_2(\omega)$ further simplifies

$$S_2(\omega) = \frac{1}{\beta} \frac{(\kappa/2)^2 - \omega^2}{[\omega^2 + (\kappa/2)^2]^2} , \quad (9)$$

and is only a κ^{-1}-order correction to $S_1(\omega)$. Generically, for many open channels the dominant part of the autocorrelation function for $\omega \sim \kappa$ is always a Lorentzian. For $\kappa \ll 1$ the tail of $S(\omega)$ crosses the ω axis at $|\omega_0| \propto \kappa^{1/2} \gg \kappa$ and then approaches zero from below. We note that in numerical simulations of the chaotic photoionization of hydrogen atom in external fields the cross-section autocorrelation was indeed found to be close to a Lorentzian

[5]. In fact, for $M \gg 1$ and $\kappa \gg 1$ it should be possible to apply semiclassical considerations and derive the autocorrelation function $S(\omega)$ from the Gutzwiller trace formula, as was done for the time-delay correlations [16,8].

We emphasize, however, that the autocorrelation function for few open channels can differ substantially from a Lorentzian. For that purpose, it is instructive to consider the single-channel case $M = 1$ where Eq. (6) can be reduced to the form:

$$S(\omega) = g\frac{\sin 2\omega}{\omega} I_1(\omega) + \frac{\sin^2 \omega}{\omega^2} \left(1 - 2g\omega I_2(\omega)\right) \qquad (10)$$

with

$$I_1(\omega) = \int_0^\infty dt \frac{\cos \omega t}{g+1+t}; \quad I_2(\omega) = \int_0^\infty dt \frac{\sin \omega t}{g+1+t} \,. \qquad (11)$$

This $S(\omega)$ diverges logarithmically for small ω, dips to a minimum below zero ("correlation hole" [11]) and then exhibits oscillatory decay to zero. As we open the system (i.e. T increases from 0 to 1), the correlation hole gradually disappears and the amplitude of oscillations diminishes. Fig. 1 shows $S(\omega)$ for several values of g. In the limit $g \to \infty$, (10) reduces to $S(\omega) = 2\delta(\omega) - Y_2(\omega)$ [11] (shown by the dashed line without the δ-function).

Parametric correlations [12] of the photodissociation cross-sections can be calculated by incorporating the usual factor of $\exp\left[-(x^2/2) f_1(\lambda, \lambda_1, \lambda_2)\right]$ (GOE) and $\exp\left[-x^2(\lambda_1^2 - \lambda^2)\right]$ (GUE) into the integrand of Eq. (5) and Eq. (6), respectively.

Another interesting quantity is the distribution function of the scaled photodissociation cross-section $\mathcal{P}(q) = \langle \delta\left(q - \sigma(E)/\langle\sigma\rangle\right)\rangle$. To calculate $\mathcal{P}(q)$ we make use of the observation [19,10] that the $N \times N$ Hermitean matrix $\hat{\mathbf{C}}\hat{\mathbf{C}}^\dagger$ has $N - M$ zero eigenvalues and that its M nonzero eigenvalues τ_c; $c = 1, ..., M$ coincide with the eigenvalues of $M \times M$ Wigner-Smith time delay matrix $Q = \hat{\mathbf{C}}^\dagger\hat{\mathbf{C}}$. Denoting the eigenvectors of $\hat{\mathbf{C}}\hat{\mathbf{C}}^\dagger$ that correspond to τ_c by $\mathbf{u}_c$, we can rewrite (3) as

$$\sigma(E) \propto \sum_c \tau_c |V_c|^2; \quad V_c = \langle g|\hat{\mu}|\mathbf{u}_c\rangle \,. \qquad (12)$$

This representation is useful in view of the known statistical properties of the time-delay matrix Q [8,14,15,20]. In particular, V_c, being proportional to the projection of $\mathbf{u}_c$ on the fixed vector $\hat{\mu}|g\rangle$, are independent Gaussian variables with the same variance $\langle g|\hat{\mu}^2|g\rangle/N$ (V_c are real for $\beta = 1$ and complex for $\beta = 2$) . We note that since the distribution of the normalized cross-section is independent of the fixed vector $\mu|g\rangle$, $\mathcal{P}(q)$ coincides with that of the quantity $\rho_n(E)/\langle\rho(E)\rangle$, where $\rho_n(E)$ is local density of states (LDOS) $\rho_n(E) = \mathrm{Im}\langle n|\left(E - \mathcal{H}_{eff}\right)^{-1}|n\rangle$ ($|n\rangle$ is a fixed vector). Special limiting cases of the LDOS distribution were studied in Refs. [18,19].

In the particular case of one open channel the time-delay distribution $\mathcal{P}_\tau(\tau)$ is known in the whole crossover regime between GOE and GUE symmetries [15]. In the GOE and GUE limits $\mathcal{P}_\tau(\tau)$ simplifies to [8]:

$$\mathcal{P}_{\tau,\beta}(\tau) \propto \tau^{-\frac{\beta}{2}+2} \int_0^\pi d\phi [g + \sqrt{g^2-1}\cos\phi]^{\beta/2} \times \exp -\frac{\beta}{2\tau}[g + \sqrt{g^2-1}\cos\phi] \,. \qquad (13)$$

Using (13) together with the known Gaussian statistics of V_c and the statistical independence of τ_c and $\mathbf{u}_c$, we find from (12)

$$\mathcal{P}_\beta(q) \propto \int_0^\infty \frac{du}{u^{3-\beta}} e^{-\frac{\beta u^2}{2}} \mathcal{P}_{\tau,\beta}\left(\frac{q}{u^2}\right) \qquad (14)$$

$$\propto \frac{1}{q^{1-\beta/2}} \int_0^\pi d\phi \frac{[g + \sqrt{g^2-1}\cos\phi]^{\beta/2}}{\Big(q + [g + \sqrt{g^2-1}\cos\phi]\Big)^{\beta+1}} \,. \qquad (15)$$

For $\beta = 1$ this expression is equivalent to that obtained in [19] by a different method.

For the general case of $M > 1$ open channels, the distribution of time-delays τ_c is known only for the special case of perfect transmission (all $T_c = 1$) [20]. In this case the LDOS distribution turns out to be intriguingly simple [19]:

$$\mathcal{P}(q) \propto \frac{q^{\frac{\beta M}{2}-1}}{(1+q)^{\beta M + 1}} \,. \qquad (16)$$

An alternative way to calculate the LDOS distribution is using the supersymmetry approach [18], in which the general case of arbitrary transmission coefficients can be evaluated for systems with broken time-reversal symmetry:

$$\mathcal{P}(q) = \delta(q-1) + \frac{1}{4\pi}\frac{\partial^2}{\partial q^2}\left[(2q)^{1/2}\int_{q_{eff}}^\infty d\lambda_1 \int_{-1}^1 \frac{d\lambda}{(\lambda_1 - \lambda)} \frac{1}{(\lambda_1 - q_{eff})^{1/2}} \prod_c \left(\frac{g_c + \lambda}{g_c + \lambda_1}\right)\right] , \qquad (17)$$

where $q_{eff} = \frac{1}{2}\left(q + q^{-1}\right)$. The integration in (17) can be performed explicitly for an arbitrary set of transmission coefficients. For equivalent channels ($g_c = g$) one finds a rather simple result:

$$\mathcal{P}(q) = \frac{q^{M-1}}{(q^2 + 2gq + 1)^{M+3/2}} \left[A_M(q^2+1) + qB_M\right] \,, \qquad (18)$$

where the coefficients A_M, B_M are given by:

$$A_M = \frac{1}{2}\left[(g+1)^{M+1} - (g-1)^{M+1}\right]\frac{(2M-1)!!}{(M-1)!}$$

$$B_M = \frac{1}{2}\left[(g+1)^{M+1} + (g-1)^{M+1}\right]\frac{(2M+1)!!}{M!} - g\frac{A_M}{M} \,. \qquad (19)$$

For the case of perfect transmission $g = 1$, we reproduce Eq. (16). In the opposite limit of an almost closed system ($g \to \infty$), we distinguish between two cases: i) the regime of isolated resonances ($g \to \infty$ at fixed M), and (ii) the regime of homogeneously broadened resonances ($g \to \infty$ and $M \to \infty$ in such a way that $M/g = \kappa/2$ is constant).

In case (i) we distinguish three different regimes for q. In the most important intermediate regime $1/g \ll q \ll g/M$, the distribution is independent of the number of open channels M: $\mathcal{P}(q) \propto g^{-1/2}q^{-3/2}$, whereas the distribution is M-dependent for very large and very small values of q: $\mathcal{P}(q) \propto g^M q^{-M+2}$ for $q \gg g/M$, and $\mathcal{P}(q) \propto g^M q^{M-1}$ for $q \ll 1/g$. In case (ii) one can use the Stirling formula in Eq. (18) to derive the distribution found in Refs. [18].

Except for the one-channel case (14), we are not yet able to derive a general formula for the GOE case (i.e. an equation analogous to (18)). However, we argue that in the limit (i) of sharply non-overlapping resonances ($g \gg M \sim 1$) the correct formula can be obtained by replacing in our GUE formula $M \to M/2$. The "superuniversal" law $\mathcal{P}(q) \propto g^{-1/2}q^{-3/2}$ is similar to that found earlier for the time-delay distribution [8,15], and is expected to be a generic feature of weakly open chaotic systems.

In conclusion, we have calculated in closed form the universal autocorrelation function and the probability distribution of the total photodissociation cross-section in the regime of quantum chaos. Our main assumptions are the applicability of RMT for describing the closed counterpart of the open quantum chaotic system, and the absence of direct field-induced transitions from the ground state to the continuum. In fact, our results hold for the bound-to-continuum strength function of an arbitrary transition operator and for any bound initial state, as long as the excited resonance states are fully chaotic.

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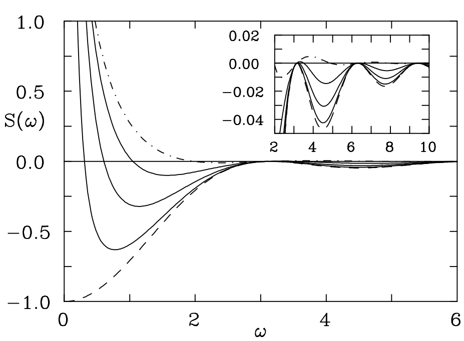

FIG. 1. The autocorrelation function $S(\omega)$ of the photodissociation cross-section vs. ω for $g \to \infty$ (closed system, dashed line), $g = 20, 5, 2$ (solid lines) and $g = 1$ (perfect transmission, dot-dashed line). As the system opens (g decreases) the minimum gets shallower. The inset shows a magnification of the oscillatory behavior of the decaying correlation.